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16. ABSTRACT

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1-Naphthol was reactive toward direct photolysis in buffered aqueous solutions (at pH 7, half-life in sunlight was about 90 min) and in cyclohexane (half-life about 15 min). The reaction rate in water increased with pH. The mechanisms of the principal photolysis pathways in both solvents did not involve singlet oxygen. In aqueous solution, the major ether-extractable product, lawsone, may have been formed by a radical process involving 1,2-naphthoquinone and superoxide as intermediates. In cyclohexane, most of the photolysis products observed were very polar. Several oxygen-containing compounds derived from the solvent were also observed. In a two-phase system including cyclohexane and pH 7 buffer, the photolysis appeared to proceed by independent mechanisms in both phases, but intermediate polar products formed in the organic layer diffused into the aqueous layer. In a system containing a surface-active material, SDS, the rate of photolysis decreased; the photoproducts were typical of those observed in cyclohexane rather than water.

The fact that the air-water interface is an area of unusual properties relative to the underlying water column has been recognized for many years. The surface tension of pure water, for example, is much greater than that of natural waters containing organic matter, even though the bulk concentration of such materials may be very low (1-10 mg/l). In fact the surface tension of many natural waters is very close to that of weakly associated liquids such as benzene. This suggests that much of the organic matter nominally dissolved in water must have considerable surface-active properties. Molecules showing such activity are those where there is a strong separation between polar and nonpolar regions within the molecular structure; a

simple example would be a long-chain fatty acid or a detergent sulfonate. Two types of surface-active molecules, wet and dry surfactants, have been distinguished (1). Wet surfactants are those in which a large portion of the molecule is physically located in the subsurface layer and only a small fraction of the surfactant projects above the surface into the air. Such molecules are normally of quite large size and include proteins, which typically have a few hydrophobic chains and a large regions of hydrophilic structure. Dry surfactants are those such as detergents, in which most of the molecule projects out of the water and only a small portion is associated with it. Although in early studies of surface microlayers, most attention was given to the determination of dry surfactants, recent work has confirmed that most of the material consists of polymeric, wet surfactants. For example, recent work on surface-active materials in freshwaters indicates that humic substances were the predominant surface-active materials in nearly all samples. Only in a few exceptional cases was the surface activity due partly to the presence of detergents (2).

Another event which will lead to a surface film on water is a spill of a hydrophobic material such as petroleum. In this case, it is likely, at least in a fresh spill, that the surface layer will be dominated by insoluble material (aliphatic and aromatic hydrocarbons) rather than surface-active material.

Many hydrophobic pollutants may tend to become more concentrated in naturally occurring microlayers, but because they are typically thin (<100 angstroms) only a very small fraction of the total pollutant load is likely to occur there. The situation is likely to be different in an oil spill event, in which the material floating on the surface of the water body is likely to form a thicker layer and also to be somewhat more stable to being disrupted by wind or wave action.

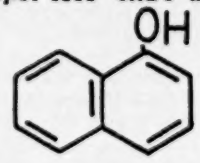
If a coherent, largely hydrophobic film exists on the surface of a water body, it may promote environmental alteration reactions of chemicals in several ways. It may act as a hydrophobic phase into which nonpolar organic compounds may partition and increase their concentration relative to the subsurface water; this may allow concentration-dependent processes to occur at faster rates. These would include oxidation reactions which require atmospheric oxygen as a reactant, since oxygen is significantly more soluble in nonpolar environments than in water. Biotic reactions may also occur faster at the air-water interface, since many types of bacteria and other microorganisms tend to concentrate there.

In order to predict the fate of an anthropogenic pollutant in natural waters, it is necessary to know how it is transported and how it is transformed, either biologically or abiotically, in the environment. For many compounds, photochemical degradation reactions are important destruction pathways. The behavior of a photochemically active compound in a surface layer, either one made up of surface-active or water-insoluble compounds, is likely to be dissimilar to its behavior in aqueous solution. Only a few studies have examined the question of the photochemical fates of organic compounds in natural surface layers: in one recent example, Zadelis and Simmons reported that the photolysis of

naphthalene in Lake Michigan microlayer material was slower by a factor of ca. 2 relative to lake water (3). As mentioned previously, the surface film formed during accidental discharges of organic liquids such as petroleum into a water body is a very different type of environment, being a mixture of compounds which are usually very insoluble. During the course of exposure of a petroleum distillate film to light and air, however, photochemical changes may take place which lead to the formation of more polar substances and thus change the nature of the "solvent." Thus, for example, when a #2 fuel oil was exposed to Pyrex filtered mercury arc light, hydroperoxides, phenols, carboxylic acids and carbonyl compounds were produced. In the absence of a water phase, the oil became cloudy due to the separation of these hydrocarbon-insoluble substances; in the presence of water, some of the reaction products were extracted into the water phase, but some remained (4). Similar observations have been noted in the field during actual oil spills; crude oil from the IXTOC blowout in the Gulf of Mexico in 1979 had both a surface crust and a brownish suspended material associated with it. The crust tended to slough off and sink (5).

Mechanistic and product distribution differences between organic solvents, organized systems such as micelles, and water may be due to many causes, such as proximity effects due to differences in solvation, retardation or promotion of photoionization and other electron-transfer processes, concentration effects caused by increased solubility in one phase of a two-phase system, selective quenching or promotion effects by codissolved solutes, or other factors.

In this paper we report some preliminary investigations of the photochemical reactions of 1-naphthol (1) in water, in organic solvents, and in two-phase systems simulating surface films. 1-Naphthol has several properties that make it a desirable probe



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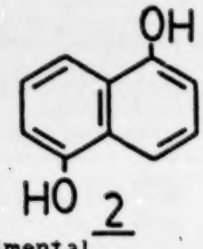
for natural photochemical processes. Although quite hydrophobic, with an octanol-water partition coefficient of about 200, it is relatively water soluble (7.7×10^{-3} M) (6). In addition, it has UV absorption maxima at 292, 308, and 322 nm, making direct photolysis possible. Furthermore, it has a relatively low-lying triplet state which has been shown to transfer energy to ground-state (triplet) oxygen, converting it to singlet oxygen ($^1O_2$); thus it may also be capable of indirect photochemical reactions.

Previous photochemical studies of naphthols have shown that 1-naphthol reacted with externally generated (methylene blue) $^1O_2$ to form 1,4-naphthoquinone (7). On the other hand, it has been observed that 1-naphthol forms the 1,2-isomer of naphthoquinone by free radical oxidations (8). Other naphthols show similar

reactions with $^1O_2$; for example, 1,5-naphthalenediol (2) forms juglone (3) with externally generated $^1O_2$, but no juglone is formed when it is treated with superoxide (O_2^-) (9).



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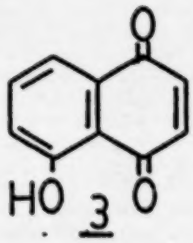

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Experimental

1-Naphthol (Aldrich) was recrystallized from water to a constant sharp melting point before use. Diethyl ether was tested for peroxides by shaking a portion with acidified KI solution and only peroxide-free ether was used for extraction. Other reagents were used as supplied. Buffers were prepared with phosphate salts, except for pHs 10.0 (bicarbonate) and 9.0 (borate). For most experiments, which were 10^{-4} M in 1-naphthol, the light source was a GE model RSM sun lamp; in use, the lamp was positioned 10 cm above the solution, which was contained in a beaker immersed in a continuous-flow water bath to maintain a constant temperature ($27\pm2^{\circ}$) and covered with a Pyrex watch glass. This arrangement gave similar UV intensities to those observed for a typical cloudless midsummer day (midmorning or midafternoon) in the northern hemisphere at 40° latitude, as measured by a digital radiometer (Ultraviolet Products, Inc., San Gabriel, CA) having separate UV-A and UV-B probes. Some kinetic experiments were performed in natural sunlight; the 1-naphthol samples, dissolved at about 10^{-5} M in appropriate solvents, were exposed in test tubes between 10 AM and 2 PM on sunny days in Athens, GA (latitude 34° N). The first-order rate constant for disappearance of 1-naphthol was determined by following the decrease in its concentration by high-performance liquid chromatography; a variable-wavelength UV detector, set at 292 nm, was employed. This rate constant was divided by the rate constant for the p-nitroanisole actinometer, determined under identical conditions, to give a relative rate constant (K_{rel}) (10). First-order kinetics were observed in all experiments, and no loss of 1-naphthol was noted in dark controls. Deaerated samples were prepared by purging with argon.

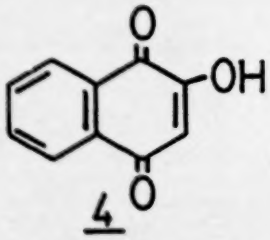
In preparative-scale (10^{-3} M 1-naphthol) experiments, an Ace-Hanovia 450-W medium-pressure mercury arc was used with a Pyrex filter sleeve and a magnetically stirred Ace water-cooled reaction vessel. In experiments involving rose bengal as a sensitizer, tungsten lamp illumination was used. Ultraviolet spectral changes were measured with a Perkin-Elmer model 552A spectrophotometer. For GC-MS analysis, a Hewlett-Packard 5985A instrument was used with a fused silica capillary column coated with a bonded nonpolar polymethyl silane phase introduced directly into the electron impact ionization source. Compounds were tentatively identified by comparison to published spectra and confirmed where possible with authentic standard materials.

Results and Discussion

Aqueous solution. During the irradiation of 1-naphthol in water, its disappearance was noted by the loss of its strong ultraviolet absorption at 292 nm. The reaction could also be followed by the increased intensity of a new peak at 262 nm. A smaller peak at 440 nm was also observed. In runs done at alkaline pH (10) it was also possible to monitor the disappearance of the enolate of 1-naphthol at 331 nm (the pKa of 1-naphthol is 9.34).

The photoreaction showed a definite pH dependence, with the faster rates occurring at higher pH (Fig. 1), indicating that the naphtholate anion may be the principal species involved in the photolysis. The anion also absorbs sunlight more strongly. The rate constant relative to the p-nitroanisole actinometer for 1-naphthol photolysis at pH 7 was about 4, corresponding to an approximate half-life of 90 min in midday summer sunlight. Control experiments for all these reaction conditions demonstrated that light was required for the reactions to occur. In the absence of oxygen, destruction of 1-naphthol still occurred, but the rate fell to approximately one-eighth of that measured in air-saturated samples.

Although many of the products of the reaction were very polar, as shown by HPLC and thin-layer chromatography, we were able to determine some of the products by extracting the aqueous solution of a preparative-scale reaction done at pH 8 with diethyl ether and analyzing the extract by gas chromatography-mass spectroscopy (GC-MS). The principal ether-soluble product was 2-hydroxy-1,4-naphthoquinone (lawsone, 4). The mass spectrum of lawsone was sufficiently characteristic to distinguish it clearly from other hydroxynaphthoquinone isomers such as juglone (11). Lawsone has also been reported previously as a product of photolysis of 1-naphthol in alkaline solution (12).



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Minor products included 1,4-naphthoquinone and a possible nonoxidative dimer with an apparent molecular weight of 288 (1-naphthol mw = 144).

It is likely that lawsone is a "second-generation" photoproduct. One mechanism by which it could be formed is the decomposition of 1,2-naphthoquinone with water. The source of the 1,2-quinone is presumed to be the reaction of 1-naphthol and superoxide radical, produced from dissolved oxygen by electron transfer from an excited state of 1-naphthol (9):

Fig. 1
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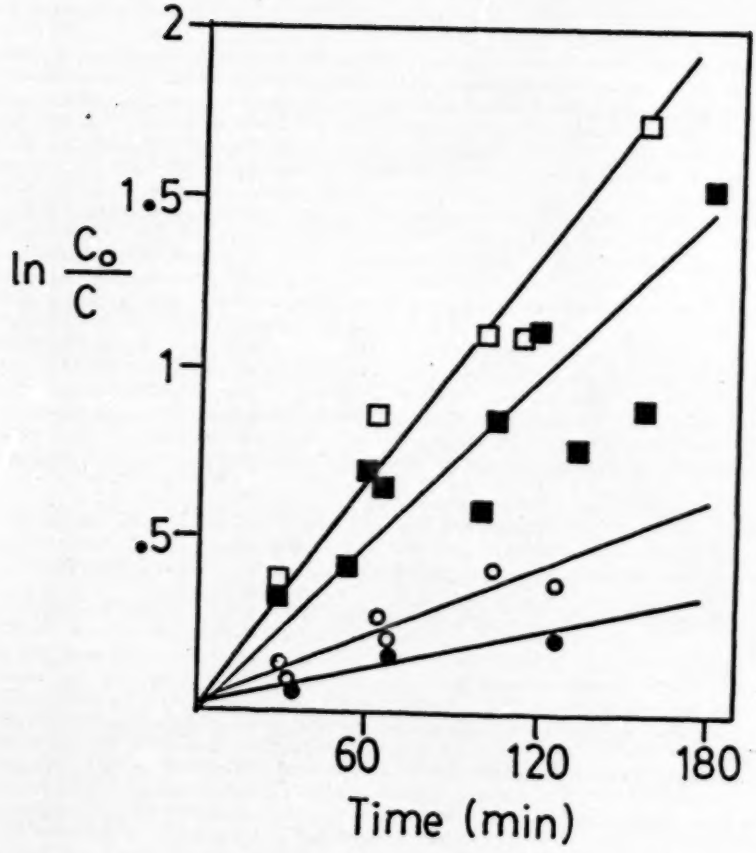
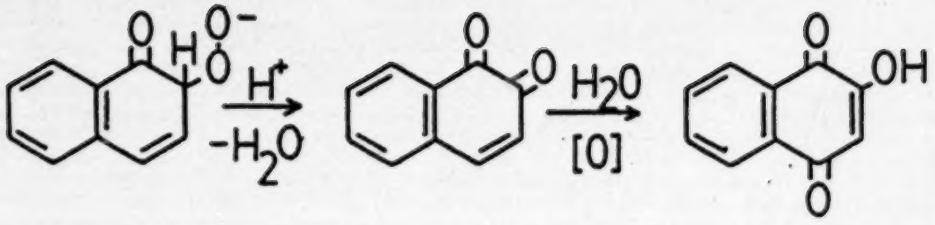


Figure 1.



In a separate reaction using rose bengal in water as a sensitizer, we confirmed that 1-naphthol exposed to externally generated $^1O_2$ gave 1,4-naphthoquinone as the sole ether-extractable product.

Cyclohexane solution. The photooxidation reactions of 1-naphthol in a hydrocarbon solvent, cyclohexane, were much different from those in water. This was demonstrated clearly by UV spectral changes during the reaction which showed only the loss of the principal 292-nm absorbance maximum of 1-naphthol; no new maxima, only increasing end absorption, were observed. Kinetic studies showed clearly that the rate of 1-naphthol photolysis in cyclohexane was far faster than in water; K_{rel} in cyclohexane was 22 (half-life about 15 min in summer midday sunlight). A preparative-scale reaction in cyclohexane confirmed that the product distribution in the hydrocarbon solvent was different. During the photolysis, an insoluble yellow residue formed. When this residue was taken up in methanol and examined by GC-MS, most of the identifiable products appeared to be derived from the solvent; such compounds as cyclohexanol and possibly 1,2-dimethoxycyclohexane were present. The principal cyclohexane-soluble product of the reaction, dicyclohexyl ether, also appeared to be derived from the solvent by a free-radical process. Another important product of this reaction, whose structure has not yet been determined, is apparently a compound retaining a monosubstituted benzene ring and having two (possibly adjacent) carbonyl groups, as shown by its mass spectrum (Fig. 2) which has major ions at m/z 77 (relative intensity 13), 105 (19), and 133 (base peak).

Two-phase experiments. We conducted a photolysis experiment in which 1-naphthol was dissolved in a small amount of cyclohexane and layered over a pH 7 buffer. The partition coefficient for 1-naphthol between these two solvents favored cyclohexane by about 5:1. In this experiment, UV spectral data indicated that to some extent the photoreactions developed product distributions that would have occurred if the other phase had been absent. Thus, in the water layer, which did not contain much 1-naphthol to begin with because of the unfavorable partition coefficient, the usual maximum at 264 nm appeared and increased in intensity as it did in the single-phase aqueous experiments. In the cyclohexane layer, the loss of the 292-nm maximum for 1-naphthol was observed as before, but a minor peak at 270 nm could also be observed. Also, the end absorption intensity decreased with time, probably because nonpolar photooxidation products were

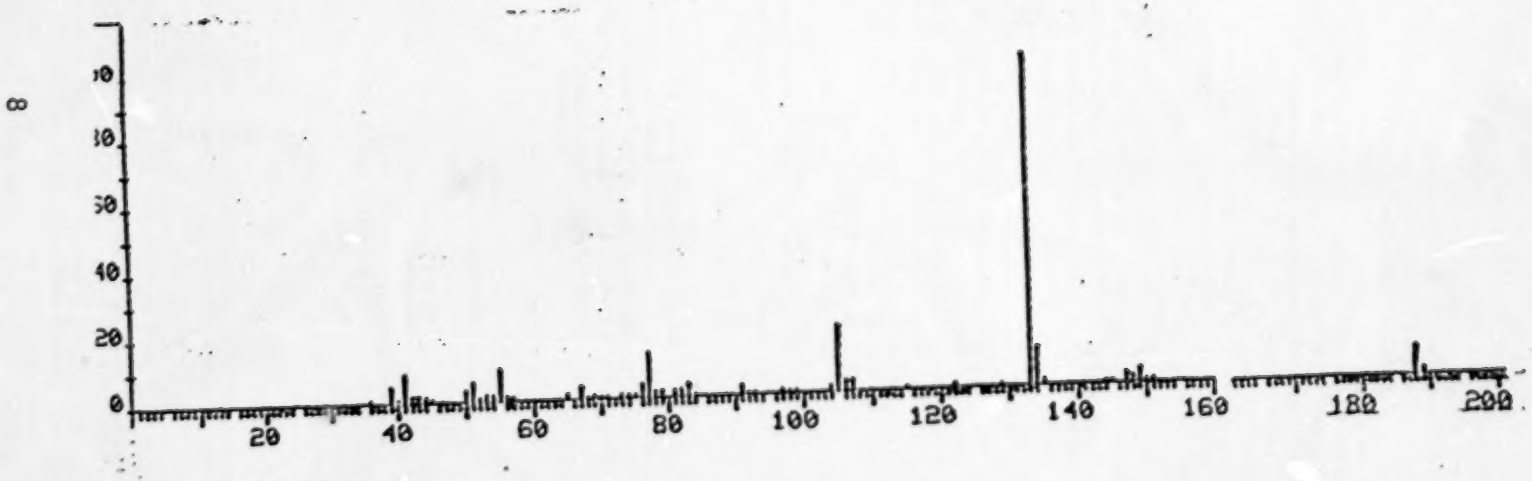
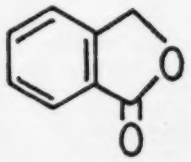


Figure 2.

diffusing into the aqueous phase. Several such products which were not identified in the cyclohexane-only system were observed in the two-phase experiment, including a dihydroxynaphthalene, phthalic anhydride, phthalide (5), and an oxidative dimer of 1-naphthol having an apparent molecular weight of 286. The latter dimer had an intense fragment ion at m/z 143, and is likely to be a one-electron ("phenol-coupling") oxidation product.



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The degradation of 1-naphthol was also investigated in the presence of a dry surfactant, sodium dodecyl sulfonate (SDS). A quantity of SDS calculated to give a surface layer of 0.1 mm thickness was used with an aqueous buffer at pH 7. The rate of this reaction was very much slower than the corresponding reaction in the absence of SDS; similar results were reported for the photodestruction of naphthalene in the presence of actual lake water surface layer material (3). The mechanistic reasons for the rate inhibitions observed in systems containing surface-active materials are uncertain. After exposure to the lamp, the reaction mixture was passed through a Dowex-2 anion exchange resin to remove the SDS, and the aqueous eluate was extracted with dichloromethane and analyzed by GC-MS. The products were the apparent benzenedicarbonyl compound with the ions at m/z 77, 105, and 133; a possible nonoxidative dimer (the same one observed in the pH 8 buffer preparative photolysis experiment) with a molecular weight of 288; and a small amount of 1,4-naphthoquinone.

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